JJP8116 P

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B41K 1/00, G03F 7/00, H01L 21/768, B41C 1/02

A1

(11) International Publication Number: WO 97/06012

(43) International Publication Date: 20 February 1997 (20.02.97)

(21) International Application Number: PCT/IB95/00609

(22) International Filing Date: 4 August 1995 (04.08.95)

(71) Applicant: INTERNATIONAL BUSINESS MACHINES CORPORATION [US/US]; Old Orchard Road, Armonk, NY 10504 (US).

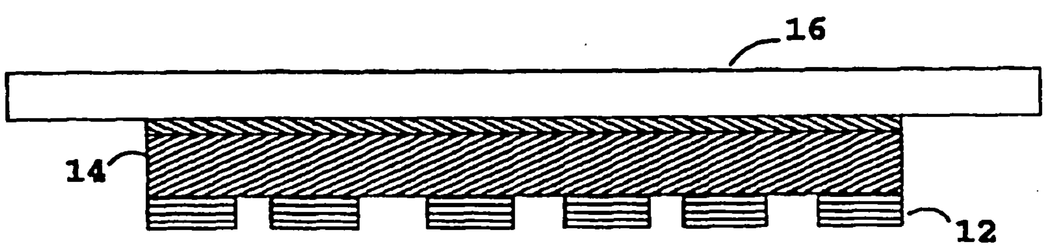
(72) Inventors: BIEBUYCK, Hans, Andre; Mythenstrasse 8, CH-8800 Thalwil (CH). MICHEL, Bruno; Obstgartenweg 13, CH-8136 Gattikon (CH).

(74) Agent: BARTH, Carl, Otto; International Business Machines Corporation, Säumerstrasse 4, CH-8803 Rüschlikon (CH).

(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: STAMP FOR A LITHOGRAPHIC PROCESS



(57) Abstract

A hybrid stamp structure for lithographic processing of features below 1 micron is described, comprising an deformable layer (14) for accommodating unevenness of the surface of a substrate and of the stamp structure itself, and a patterned layer (12) in which a lithographic pattern is engraved. The stamp structure is further enhanced by comprising a third layer (16), which acts as rigid support for the stamp, thus preventing an undesired deformation of the stamp under load.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

DESCRIPTION

Stamp for a Lithographic Process

The present invention is directed generally toward a lithographic process. More particularly, it relates to an elastomeric stamp for use in such a lithographic process.

BACKGROUND OF THE INVENTION

Since the emergence of integrated circuits (ICs) and micromechanical devices, optical lithography has been crucial for the purpose of their mass production: Its convenience, parallel operation and resolution has created a huge market. Fabrication of devices with ever smaller dimensions, necessary to satisfy the increasing demands of storage and computation, becomes increasingly problematic with visible light as processes steadily reaching fundamental limits, predominantly set by diffraction. This realization triggered intense research in UV, X-ray, e-beam, and Scanning Probe (SP) lithography. These methods deliver high resolution with varying success and their economics remain, at best, uncertain. Reasons for these uncertainties include limitations due to wavelength dependent phenomena, the slow writing speeds of e-beam and SP lithographies, and challenges in finding appropriate resists.

A separate and related limitation of current lithographies is the complexity of processes required for pattern transfer; lithography today relies on transfer of material from the liquid or gas phase using masks to protect certain regions of the substrate so that devices are filled in more than assembled.

An alternative approach to lithography has been published by A. Kumar and G.M. Whitesides in: Appl. Phys. Lett. 63 (14), 4 October 1993, pp. 2002-2004. In this process, referred to as stamp lithography, stamps are fabricated by casting poly(dimethylsiloxane) (PDMS) on a master with a negative of the desired pattern. The PDMS stamp is peeled away from the master after curing and exposed to an "ink" transferred to the substrate by transient contact with the stamp. The elastomeric nature of the PDMS allows contact even on rough or curved surfaces. According to this method, features between 1 and 100 microns are achieved. For larger stamps and larger features (1 cm to 200 microns), the pattern is directly etched into the stamp by conventional UV lithography using a mild soap solution for dissolving those regions previously exposed to the UV light. When applying this method to lithography with submicron features, it was found that no reproducible results necessary for mass-production of ICs were attainable with a type of stamp as propagated by Kumar et al. A major limitation of this method of pattern transfer is the elastomer used as carrier of the pattern. This material is deformable so that repeated, accurate transfer of the pattern to the substrate with high resolution, as necessary for practical lithography, is not possible.

Therefore, it is seen as an object of the invention to improve the method described by Kumar et al. such that stamp lithography can compete with the current state-of-the-art lithography. Particularly, features of 0.1 to 1 microns width should be achievable in a reproducible manner, suitable also for covering conventional wafer sizes.

SUMMARY OF THE INVENTION

The object of the invention is achieved by a stamp as set forth in the appended claims. The new composite stamp avoids the limitations of the prior art stamp. Using the new stamp, feature sizes or a "design rule" of below one micron can be achieved in a reproducible manner. Due to its

novel structure it can be optimized for matching all important properties, i.e., rigidity, conformal contact, and accurate pattern transfer, simultaneously.

It is seen as an important feature of the invention that the stamp comprises an deformable or elastic layer for conformal contact, accommodating the fluctuations of the thickness of the substrate and impurities on its surface, and a second (patterned) layer, which carries the desired pattern. This layer is preferably made of a material having a Young's modulus in the range of 10^4 to 10^7, more preferably of $0.25 * 10^6$ to $5 * 10^6$ dyne/cm^2. Material having this property can be poly(butyldiene), poly(dimethylsiloxane), poly(acrylamide), poly(butylstyrene) and co-polymers of these types. It is desirable to optimize the properties of the elastic layer such as to control the desired amount of flexibility.

A stamp made in accordance with the invention has several advantages over the known uniform elastomeric stamp. The materials of both layer can be optimized to a large extent independently of each other. Thus it is desirable to have a patterned layer to which submicron features can readily be written by a lithographic process. The patterned layer should also easily adhere to or absorb a specific "ink" material. It is further desirable to produce the patterned layer from a preferably non-deformable material which accurately preserves the pattern features even after repetitive application in the lithographic process. The patterned layer can be made of an material with a high Young's modulus, preferably above 10^6 dyne/cm^2. Suitable materials could be organic, such as poly(styrene) or poly(methylmethacrylate), metallic, such as gold, platinum, palladium, nickel, titanium and oxides thereof, or inorganic insulators like alumina, silicon, silica, or perovskites, depending on the desired properties and application.

In a preferred embodiment of the invention, the elastomeric layer is mounted onto a rigid support structure being even within a tolerance of less than 10 microns, preferably in the range of 1 micron to 1 nm. A preferred support material has a thermal expansion coefficient close to the one of the substrate material. The support is preferably chosen from a group consisting of glass, quartz glass, rigid plastics material, or the substrate or wafer material, e.g. silicon. When mounted on a support structure, the elastic layer itself can be thin. Its thickness lies preferably in a range of 10 to 1000 microns. In this range of thickness, any deformation can be accommodated by the elastic layer, while the features of the pattern maintain their dimensions even when the stamp is pressed during the lithographic process. When protruding self-alignment means are used, as are described below, the thickness of the elastic layer may preferably be chosen from a range of 10 to 10000 microns. Obviously, a support structure as described above can also be advantageously applied to the known one-layer stamps as described by Kumar et al.

In a further preferred embodiment, the stamp comprises means for achieving a self-alignment. The means could either comprise key-and-lock type topological features, e.g. cone- or pyramid-shaped protrusions and holes, which after a sufficiently accurate pre-positioning by stepping drives guide the stamp into the desired final position. A preferred means for self-aligning the stamp and the substrate however exploits surface tension gradients provided on the surface of the stamp and/or substrate. These gradients are, for example, achieved by distributing pads on the surface of substrate and stamp, said pads being characterized by a modified surface providing a higher affinity to a liquid, e.g. oil or water.

These and other novel features believed characteristic of the invention are set forth in the appended claims. The invention itself however, as well a preferred mode of use, and further objects and advantageous thereof, will best be understood by reference to the following detailed description of

illustrative embodiments when read in conjunction with the accompanying drawings.

DESCRIPTION OF THE DRAWINGS

The invention is described in detail below with reference to the following drawings:

FIG. 1A - 1D illustrate basic steps of a first method for producing a stamp according to the invention.

FIG. 2A - 2D illustrate basic steps of a second method for producing a stamp according to the invention.

FIG. 3 illustrates a key-and-lock type means for self-alignment of a stamp and a substrate.

Figs. 4 A,B illustrates means for self-alignment of a stamp and a substrate based on a surface tension gradient.

Figs. 5 - 7 illustrates the basic steps of preparing a stamp and a substrate for stamp lithography.

FIG. 8 illustrates the use of a new stamp in accordance with the invention in a lithographic process.

MODE(S) FOR CARRYING OUT THE INVENTION

A first example of the invention is now described, referring to figures 1A to 1D. The process starts with a silicon wafer **10**, which provides a very flat surface. The surface is coated with a thin layer **11** of perfluorinated silane.

The perfluorinated silane prevents an adhesion or bonding of the following layers to the silicon surface. Next, a layer of a brittle material capable of accurately holding a pattern is deposited onto layer **11**. The brittle material is either poly(methylenmethacrylate)(PMMA), which is deposited by spincoating or polysilicon which is deposited by chemical vapor deposition. Both deposition methods are well known in the art. The layer thickness is chosen in dependence of the average features size, the so-called "design point" in a ratio of approximately 1:1. The layer **12** is structured by conventional UV lithography, or alternatively by e- beam lithography. Spacer elements **13** are positioned on the wafer **10**. Into the volume defined by the spacer elements, pre-polymers of poly(dimethylsiloxane)(PDMS) are cast to form, after a curing process, an elastic layer **14** over the patterned PMMA or polysilicon **12**. A second silicon wafer **16** is lowered onto the spacer elements, squeezing any surplus amount of PDMS through gaps between the spacer elements. This second silicon waver is pre-treated with an olefin terminated silane which provides a glue-like layer **15** to bond to the PDMS. By lifting the assembly, the lower layer **10** of silicon is separated from the rest. Thereafter, the patterned layer of PMMA or polysilicon is developed by dissolving or etching the exposed areas, resulting in a composite stamp structure as illustrated by Fig. 1D.

An additional layer **17** can be introduced between the patterned PMMA layer **12** and the deformable layer **14** to provide an additional support for the pattern after its development. In the example as illustrated by Fig. 1E, this intermediate layer consists of PMMA. However this layer can be replaced by a layer of indium tin oxide (ITO), an electrically conductive material. This additional layer besides providing an enhanced stability of the pattern (and electrical conductivity) also prevents the elastic material of layer **14** from penetrating through the openings of the patterned layer **12**.

A second method for producing a composite stamp is illustrated by Figs. 2A - 2D. First, a master substrate **20** is provided by any conventional lithography method (or by the stamping lithography describe herein). The

master pattern is treated with perfluorinated silane **21** as a separating agent. Thereafter, a layer **22** of PMMA is spincoated onto the assembly. The following steps (Figs. 2C, 2D) correspond to those of the previous example. By lifting the assembly, the stamp and the master are separated, leaving the master **20** for further replication of the stamp.

Referring now to Fig. 3, a first self-alignment means on substrate **30** and stamp **31** is shown, comprising of wedge-shaped protrusions **311** of PMMA exceeding the features of the lithographic pattern **312**. The protrusions **311** fit exactly into corresponding recesses **301** of the substrate. This can be achieved by employing the same alignment stamp when producing the recesses **301** in the substrate and in the master from which the stamp is replicated. Provided that the substrates are made of the same material and all etching parameters are equal, the wedges **311** and the recesses **301** match exactly. This concept of providing matching marks on the substrate and on the stamp is described in further detail below.

Whereas in the lock-and-key type of self-alignment the geometrical shape of the features, e.g. the tilted sidewalls, cause a fine-adjustment of the stamp and the substrate, the following example of self-alignment means, as being illustrated by Figs. 4A and 4B, is based on the property or tendency of a liquid to minimize its surface. With hydrophilic pads **401, 411** on the surfaces of both, the substrate **40** and the stamp **41**, together with a controlled amount of moisture, leading to the formation of small droplets on and between these pads, an efficient self-aligning mechanism is realized: In case of a small misalignment of the stamp with respect to the substrate, a sandwiched droplet **420** provides a restoring force back to the regular shape, thereby moving the stamp into its desired position. The droplet can be generated in a controlled manner by exposing the pads to a moisturized inert gas (humidified nitrogen). It should be noted that the features of Fig. 4 are as all other figures not drawn to scale. The size of the droplet should be approximately of the order of the cubic of the design rule.

The efficacy of this method can be increased by depositing a hydrophobic zone **402** around each of the pads **401** or by placing the pads on post-type supports **412** as shown in Fig. 4B. Another advantageous property of the sandwiched droplet **420**, also illustrated by Fig. 4B, is its acting as a elastic cushion when pressure is exerted upon the assembly. Thus, the stamp immediately is lifted from the substrate when releasing the exerted pressure by the spring forces of the deformed droplets **420** and/or posts **412**.

Self-alignment means should be placed in the vicinity of cleavage lines of the wafer thus ensuring that a minimum of utilizable wafer area is occupied. The lateral dimensions of the self-alignment means again are in the order of the design rule.

The following figures are to illustrate the basic steps of preparing an aligned assembly consisting of a wafer substrate and one or several stamps.

In a first step, an alignment master **50** as shown in Fig. 5 is prepared, which carries recesses **501** at preselected positions, which preferably are located at regions designed to be the cleavage lines of the wafer to be manufactured. Of the alignment master several alignment stamps **61** can be produced as replicas carrying alignment marks **611** (Fig. 6A). To provide hydrophilic pads on a wafer, a replica of the alignment stamp is inked with 16-mercaptohexadecanol acid **612** or, alternatively, with 16-mercaptohexadecanol, which is transferred by stamp contact printing (Fig. 6B) onto a wafer **60** covered with a thin gold film **601**, which adheres to the thiol. The uncovered gold film is then removed, exploiting the thiol pad **602** as protective coating. After evaporating another gold film while shielding the neighborhood of the pads by a mask, the wafer is prepared for further processing (Fig. 6C).

Referring now to Fig. 7A, a silicon stamp master **70** is shown coated with perfluorinated silane **702**. Prior to the lithographic pattern **703**, alignment recesses **701** are marked and etched into the silicon using an alignment

stamp drawn from the alignment master as shown in Fig. 5. The lithographic pattern **703**, produced by conventional e-beam lithography, is written using coordinates relative to the alignment marks **701**. By using the same alignment stamp for different stamp masters and by positioning the lithographic pattern relatively to the alignment marks, stamps with different lithographic patterns can be manufactured. These stamps can replace the masks used in the known lithographic methods. Due to the above described manufacturing procedure, these stamps are inherently aligned to each other. By using the same alignment stamp for the wafer, as is described above when referring to Figs. 6A-6C, all such produced stamps can be placed in a self-aligning fashion onto the wafer.

The stamp master is spincoated with the pattern layer of the composite stamp **712** (PMMA), shown in Fig. 7B. Before applying the elastic layer **714** (PDMS), the resist within the recesses **701** is exposed, etched away and replaced by a thin layer of gold **718** (Fig. 7C). Then spacer elements **713** are installed at the perimeter of the stamp master, and the thus created volume is filled with the elastomer **714** (Fig. 7D). As described above, a second silicon plate **716** is applied as supporting layer. After lifting the stamp assembly and trimming of its rim (Fig. 7E), the stamp **71** is dipped into a solution of carboxyl (COOH) terminated thiols **705** to apply hydrophilic pads **718** to the alignment protrusions **711**. The preparation of the stamp **71** is completed by wetting the layer **712** with lithographic pattern with the substance **719** to be transferred to the wafer (Figs. 7F, 7G).

For the actual lithographic process, as illustrated by Fig. 8, a moisture carrying gas is blown over the hydrophilic pads **601** on the surface of the wafer **60** as prepared in a previous step (Fig. 6C). The stamp **71** is positioned by known alignment means such that its hydrophilic pads **718** are in approximate juxtaposition of those on the wafer. The final alignment is then achieved by the surface tension of the droplets **820** sandwiched between the hydrophilic pads.

The lithographic pattern is transferred to the wafer **60** by exerting pressure on the stamp **71** until the wetted layer **712** touches the surface layer **601** of the wafer. The substance **719**, which could be a reactant, etchant, protective coating, etc., is then transferred at all areas of contact.

CLAIMS

1. Stamp structure for a lithographic process, comprising a deformable layer (14; 24) of a first material for making a conformal contact between the surface of a substrate (30; 40; 60) and of said stamp structure, and a patterned layer (12; 22) of a second material with a lithographic pattern to be transferred to said substrate.

2. The stamp structure of claim 1, further comprising a rigid support (16; 26) for preventing an undesired deformation of the deformable layer under a load.

3. The stamp structure of claim 1, further comprising self-aligning means (301, 311; 401, 411, 420) for an accurate relative positioning and/or deformation of the substrate (30; 40) and the stamp structure (31; 41) during the lithographic process.

4. The stamp structure of claim 3, wherein the self-aligning means comprises protruding elements (311) and corresponding recess elements (301), preferably with tilted sidewalls.

5. The stamp structure of claim 3, wherein the self-aligning means comprises a surface tension gradient.

6. The stamp structure of claim 5, wherein surface tension gradient is achieved by pads (401, 411) having a higher affinity to a liquid than their surrounding areas.

7. Use of a stamp structure in accordance with claim 1 for submicron lithography.

8. Lithographic process comprising the steps of

- preparing a stamp structure comprising a deformable layer (14; 24; 714) of a first material for making a conformal contact between the surface of a substrate (30; 40; 60) and of said stamp structure, and a patterned layer (12; 22; 712) of a second material with a lithographic pattern to be transferred to said substrate;

- applying a substance (719) to said patterned layer; and

- bringing said patterned layer into a conformal contact with said surface of said substrate.

9. The lithographic process of claim 8, further comprising the steps of

- preparing a master alignment stamp (60) carrying alignment marks (611); and

- using said alignment master for reproducing self-alignment means (602; 718) on the substrate and the patterned layer at precisely corresponding positions.

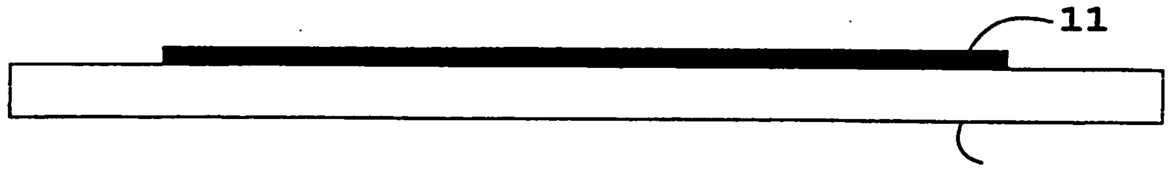


Fig.1A

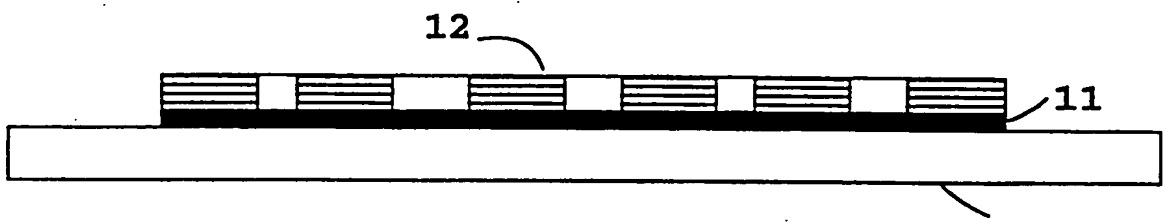


Fig.1B

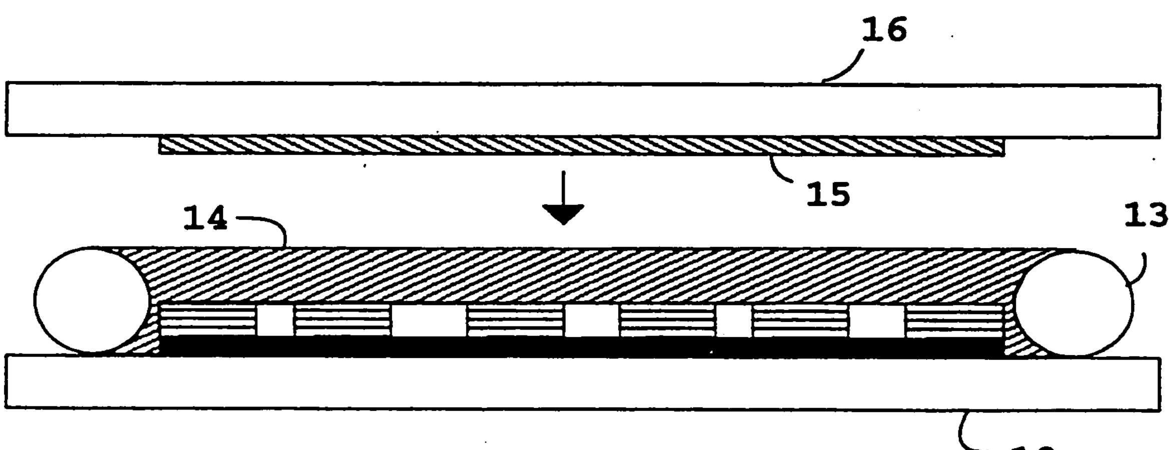


Fig.1C

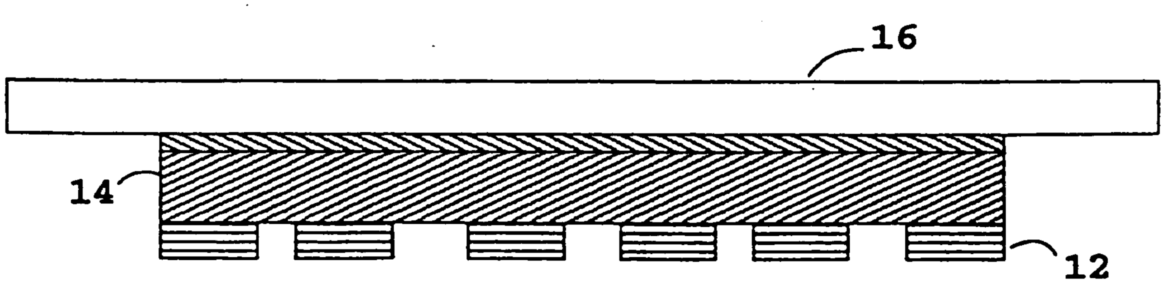


Fig.1D

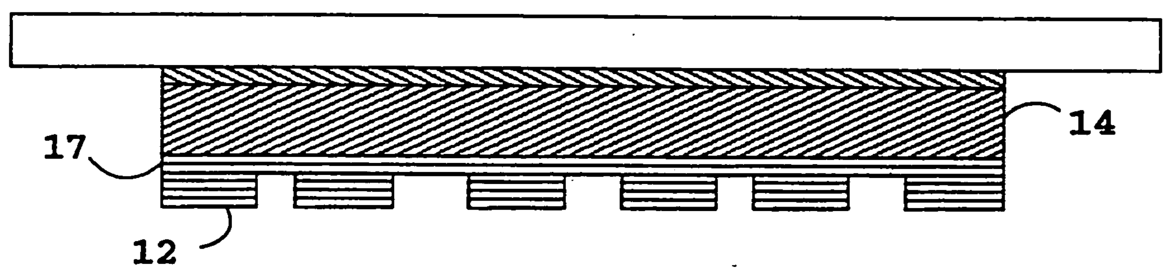


Fig. 1E

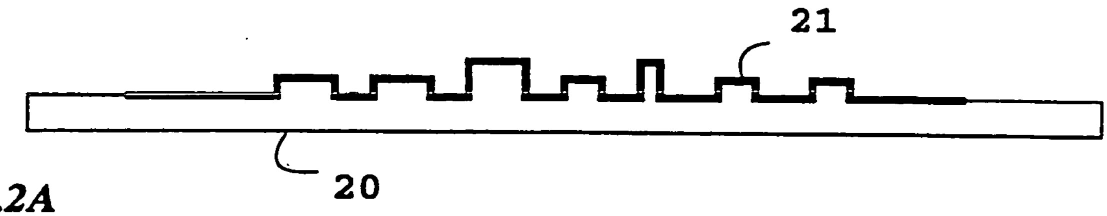


Fig.2A

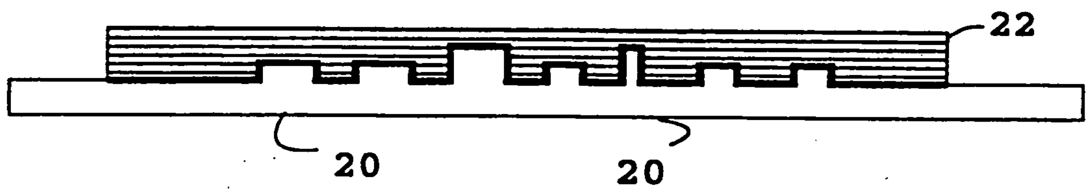


Fig.2B

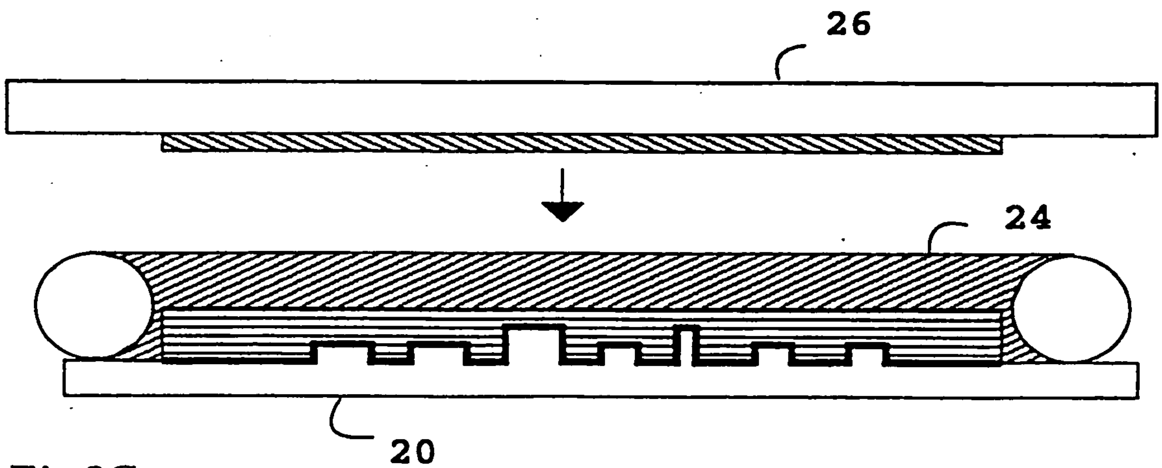


Fig.2C

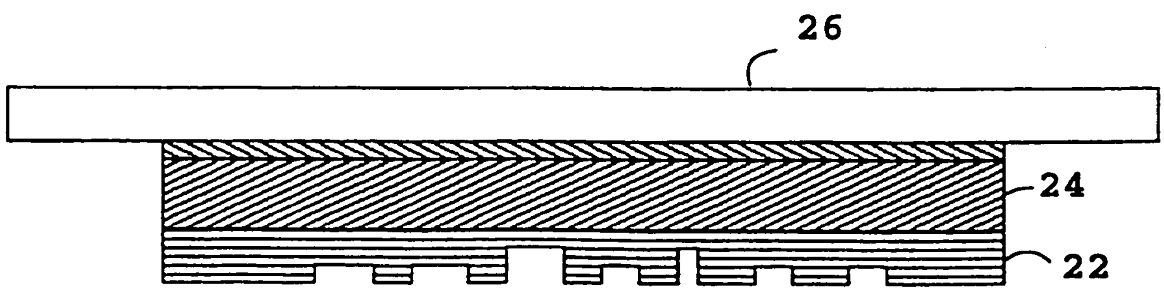


Fig.2D

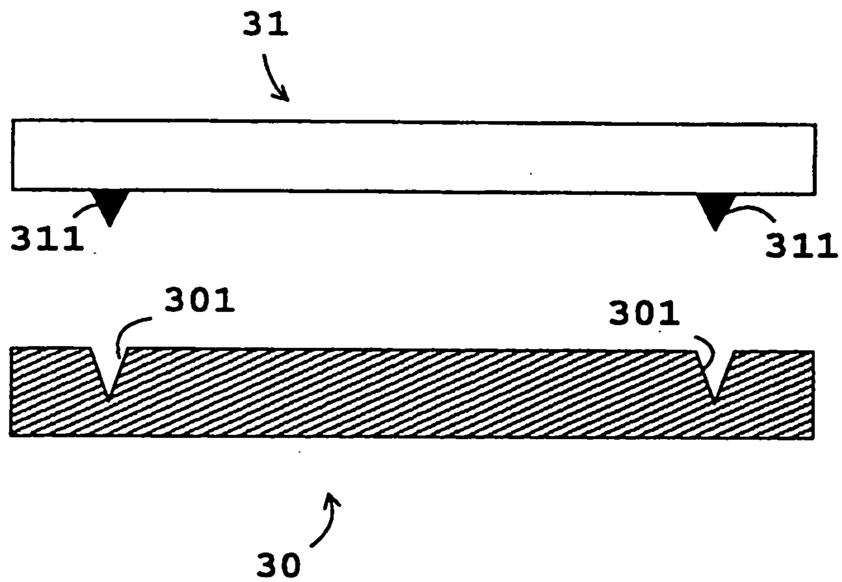


Fig.3

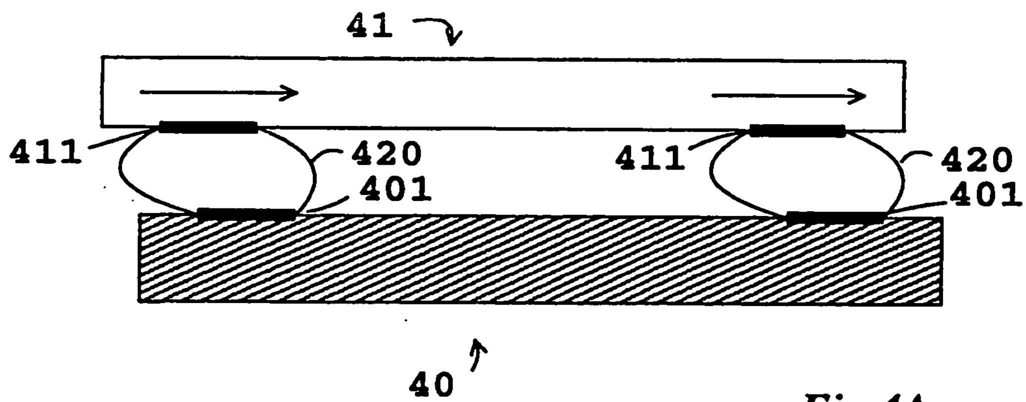


Fig.4A

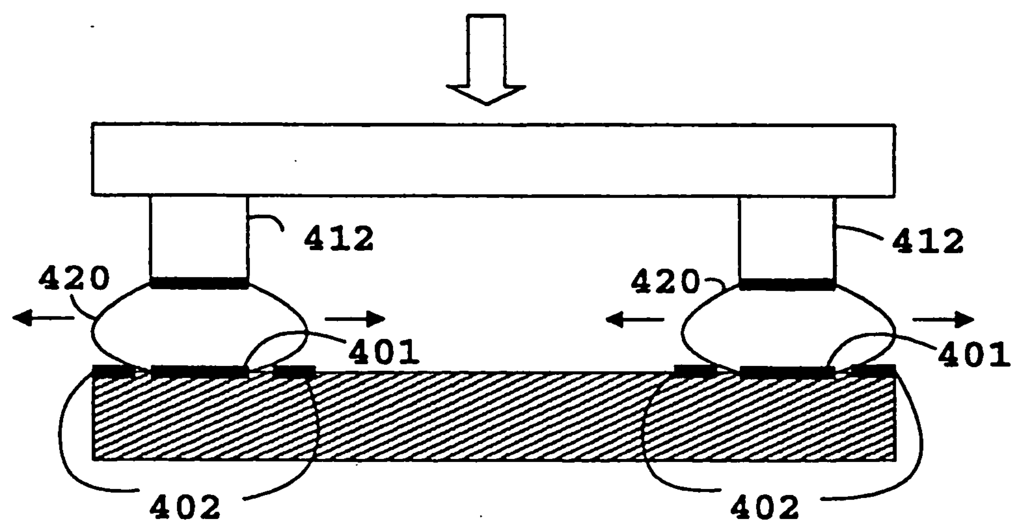


Fig.4B

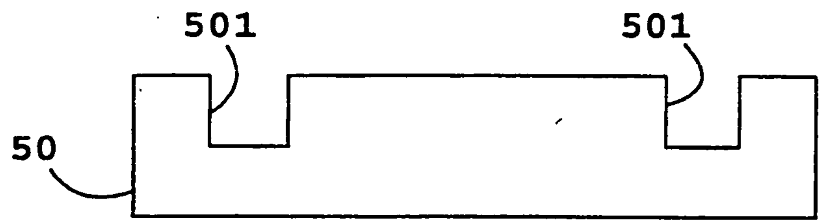


Fig.5

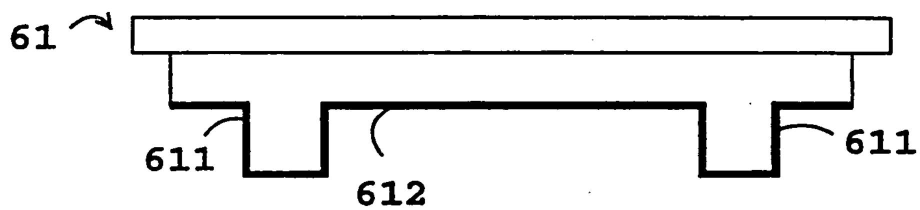


Fig.6A

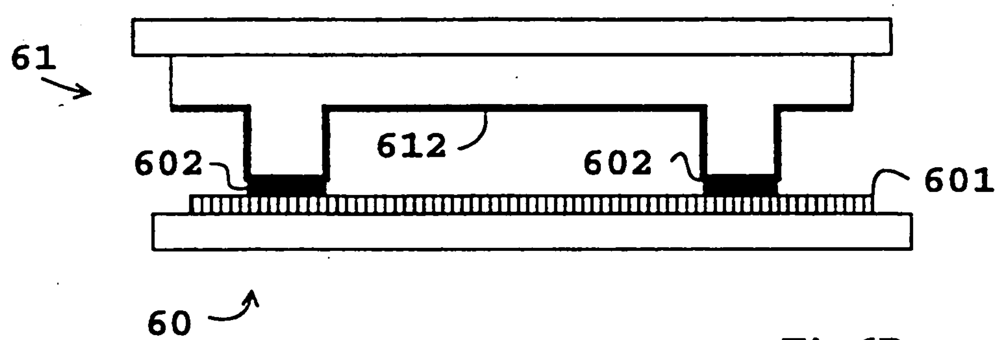


Fig.6B

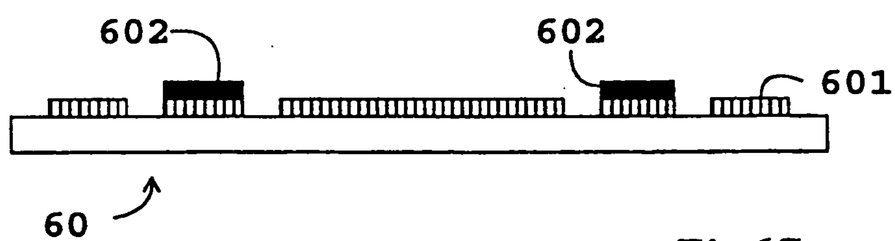


Fig.6C

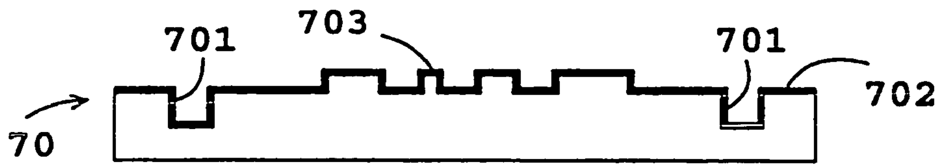


Fig.7A

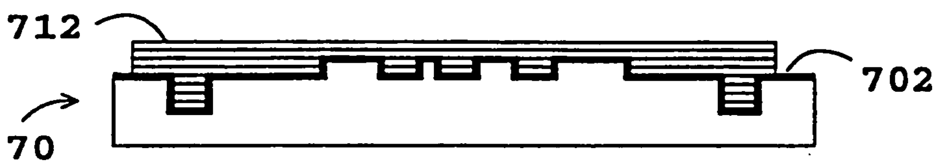


Fig.7B

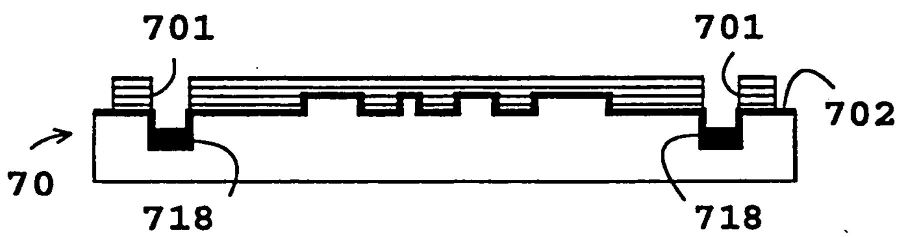


Fig.7C

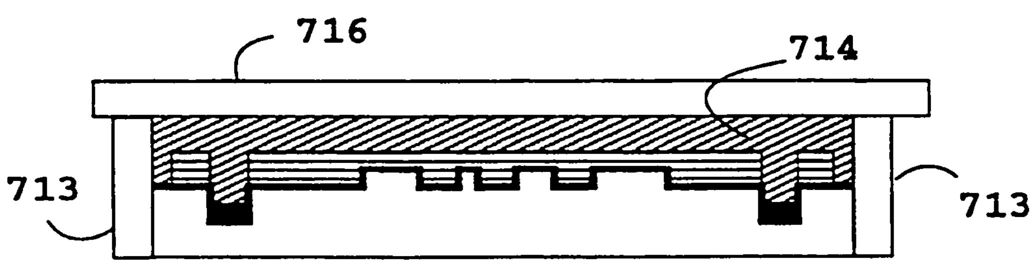


Fig.7D

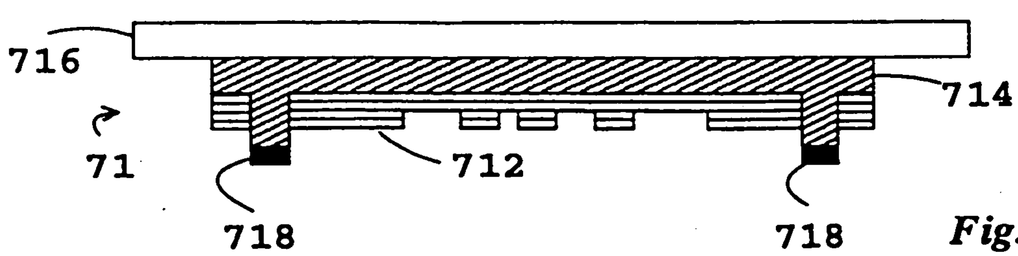


Fig.7E

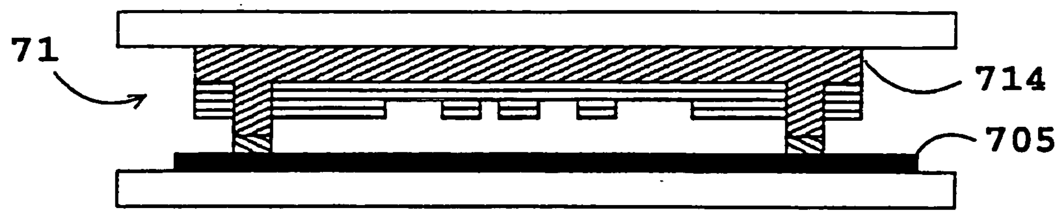


Fig.7F

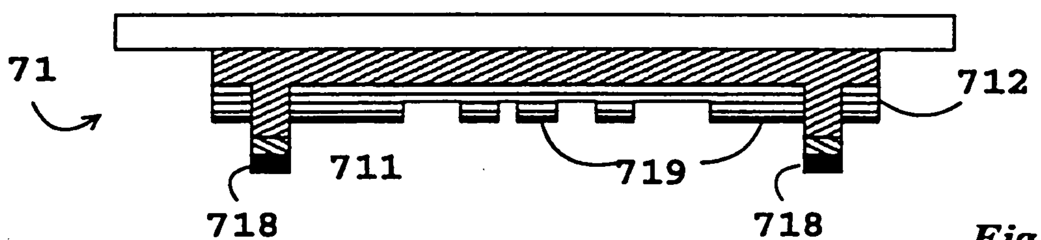


Fig.7G

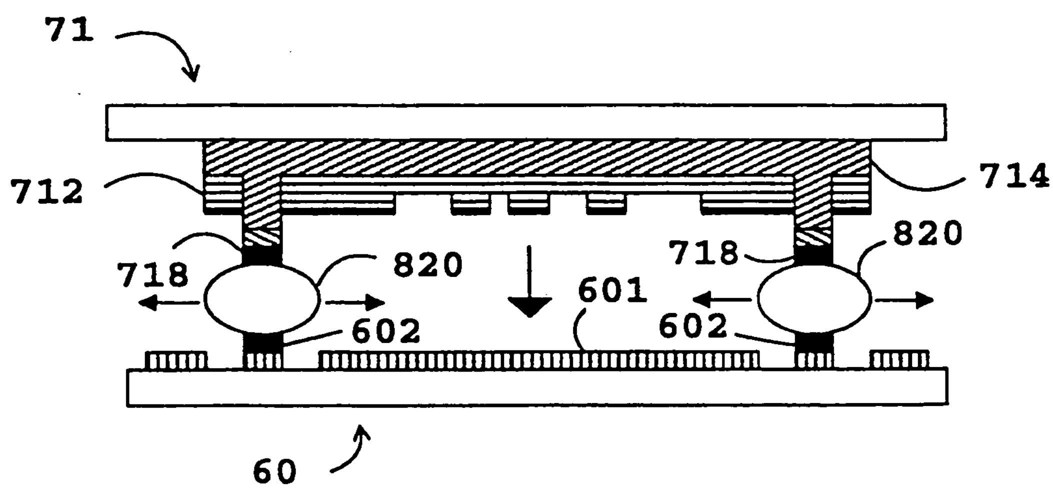


Fig. 8

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 95/00609

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41K1/00 G03F7/00 H01L21/768 B41C1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41K G03F H01L B41C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ADVANCED MATERIALS, vol. 7, no. 5, May 1995, WEINHEIM DE, pages 471-473, XP000533523 Y. XIA ET AL.: "Reduction of Size of Features of Patterned SAMs Generated by Microcontact Printing with Mechanical Compression of the Stamp" see the whole document ---	1-9
Y	FR,A,2 663 760 (AMRI DAHBIA) 27 December 1991 see page 2, line 3 - line 6 ---	1-9
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 24, no. 1B, June 1981, NEW YORK US, pages 637-638, XP002001686 "Store Logo Stamp Printer" see the whole document ---	3

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

2

Date of the actual completion of the international search	Date of mailing of the international search report
26 April 1996	07.06.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rasschaert, A

INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT/IB 95/00609

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 26, no. 11, April 1994, NEW YORK US, pages 5993-5994, XP002001687 M.J. BRADY ET AL.: "Self-aligned Optical Fiber/Laser Structure" see the whole document ---	4
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 29, no. 2, July 1986, NEW YORK US, pages 560-562, XP002001688 "Method for Assembling a multilayer planar object" see the whole document ---	4
A	EP,A,0 583 714 (DU PONT) 23 February 1994 see the whole document ---	1
A	ADVANCED MATERIALS, vol. 7, no. 7, July 1995, WEINHEIM DE, pages 649-652, XP000520481 J.WILBUR ET AL.: "Lithographic Molding : A convenient Route to Structures with Sub_Micron Dimensions" see the whole document ---	1-9
A	GB,A,1 431 462 (AGFA GEVAERT AG) 7 April 1976 see the whole document -----	1

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 95/00609

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2663760	27-12-91	NONE		
EP-A-0583714	23-02-94	US-A-	5270078	14-12-93
		CA-A-	2103863	15-02-94
		JP-A-	6219069	09-08-94
GB-A-1431462	07-04-76	DE-A-	2253944	09-05-74
		BE-A-	806432	24-04-74
		CA-A-	1005329	15-02-77
		CH-A-	582723	15-12-76
		FR-A-	2206704	07-06-74
		JP-A-	49079240	31-07-74